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COMPREHENSIVE ANALYSIS OF AIRBORNE CONTAMINANTS FROM RECENT SPACELAB MISSIONS

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ABSTRACT

The Shuttle experiences unique air contamination problems because of microgravity and the closed environment. Contaminant build-up in the closed atmosphere and the lack of a gravitational settling mechanism have produced some concern in previous missions about the amount of solid and volatile airborne contaminants in the Orbiter and Spacelab. Degradation of air quality in the Orbiter/Spacelab environment, through processes such as chemical contamination, high solid-particulate levels, and high microbial levels, may affect crew performance and health. A comprehensive assessment of the Shuttle air quality was undertaken during STS-40 and STS-42 missions, in which a variety of air sampling and monitoring techniques were employed to determine the contaminant load by characterizing and quantitating airborne contaminants. Data were collected on the airborne concentrations of volatile organic compounds, microorganisms, and particulate matter collected on Orbiter/Spacelab air filters.

The results showed that the STS-40/42 Orbiter/Spacelab air was toxicologically safe to breathe, except during STS-40 when the Orbiter Refrigerator/Freezer unit was releasing noxious gases in the middeck. On STS-40, the levels of airborne bacteria appeared to increase as the mission progressed; however, this trend was not observed for the STS-42 mission. Particulate matter in the Orbiter/Spacelab air filters was chemically analyzed in order to determine the source of particles. Only small amounts of rat hair and food bar (STS-40) and traces of soiless medium (STS-42) were detected in the Spacelab air filters, indicating that containment for Spacelab experiments was effective.

1.0 INTRODUCTION

Shuttle air quality may be degraded by an accumulation or an abrupt release of contaminants in the cabin atmosphere. Since most nonmetallic materials continuously release (or offgas) trace amounts of volatile contaminants, build-up of offgas contaminants from flight hardware materials could reach harmful levels inside the closed environment of the Shuttle. It has been observed in "tight" or "sick" buildings that inhalation of low concentrations of volatile organic compound mixtures may have adverse effects on memory.[1] Events, such as overheating of insulation materials, release of utility chemicals (i.e., refrigerant, fire extinguishant), or chemical spills from payload experiments, have the potential to quickly release high concentrations of volatile contaminants into the cabin atmosphere. These abrupt releases may expose crewmembers to high levels of toxic contaminants, resulting in eye, skin, or respiratory tract irritation and/or systemic toxicity. Accumulation of airborne microorganisms in the closed environment increases the risk of contracting in-flight infections, as observed in

early Apollo missions.[2] Because of the microgravity environment, particles of food, paint chips, lint, dust, skin flakes, and hair are suspended in the Shuttle air before they are trapped onto the air filters. These free-floating particulates are a potential source of eye, skin, or respiratory tract irritation.

Preflight measures to control airborne contaminant levels include evaluation of flight hardware materials and containment of payload experiments and determination of microbial levels inside the Shuttle. Preflight offgas testing is required for all hardware in the flight certification process. Articles or materials that might release toxic amounts of chemicals into the Shuttle atmosphere are identified in preflight offgas testing. Hazards from payload and utility chemicals and materials are evaluated, and appropriate containment is recommended according to the toxicity and amount at risk for release into the cabin atmosphere. Two to three weeks before the launch, Orbiter air and preselected surfaces are sampled for microbial contaminants. Microbial levels greater than 1000 colony forming units per m^3 of air indicate that further cleaning of Orbiter surfaces or air ducts is required, depending on the location of the contamination. Volatile contaminants are evaluated in terms of their spacecraft maximum allowable concentrations (SMACs). SMACs are evaluated and set for each volatile contaminant, thus providing safe crew exposure limits. Limits have also been set for airborne solid particulates; for flights greater than one week, the NASA Panel on Airborne Particulate Matter in Spacecraft has recommended concentrations of 200 $\mu g/m^3$ for particles less than 10 μm in aerodynamic diameter (AD) plus 200 $\mu g/m^3$ for particles 10 to 100 μm in AD.[3]

During the flight, air quality is monitored via archival methods for volatile, microbial, and particulate contaminants. Volatile contaminants are collected from the air using "grab" air and solid sorbent sampling methods for ground-based gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) analyses. Microbial contaminants sampled from the cabin air using a centrifugal air sampler are deposited on agar-media and subsequently incubated for ground-based analyses. Particulate levels have been monitored on STS-32/40 missions using the Shuttle Particle Samplers and Shuttle Particle Monitor. Results from these missions have shown that the total particulate concentrations (size range < 2.5 to > 100 μm in AD) of 33 $\mu g/m^3$ (STS-40)[4] and 56 $\mu g/m^3$ (STS-32)[5] in Shuttle air were well below the 200 $\mu g/m^3$ limit.

Special particulate studies were initiated following the STS-40 and STS-42 missions to determine the effectiveness of containment of particulate matter generated in Spacelab experiments. On Spacelab missions, there was a concern that experiment-generated particles might add to the normal particulate load. Since released particulates from the experiments would also be trapped on the Orbiter/Spacelab air filters, it would be possible to collect and analyze such particles from the filter debris. If released into the cabin atmosphere, biological-type particles produced in Spacelab experiments may be a potential inhalation hazard and/or spread infection. Positive identification of particles by visual means is not always possible, therefore, pyrolysis-gas chromatography/mass spectrometry (PY-GS/MS) was adapted for the analysis of organic particles. By heating the particle to a pyrolysis temperature of 600 °C, the particle is converted into a mixture of chemical components of lower mass. The pyrolysis spectrum obtained by PY-GC/MS contains "marker" compounds, which are specific to the type of particle under analysis and can be used to identify an unknown particle. Therefore, the main purpose of this particulate study was to determine, through microscopic and analytical chemistry methods, if particles produced in Spacelab experiments were escaping into the Shuttle atmosphere.

2.0 MATERIALS AND METHODS

2.1 VOLATILE CONTAMINANT SAMPLING

2.1.1 Sampling Cylinders

Stainless steel sampling cylinders were used to collect 300 ml "grab" samples of air inside the Shuttle. By collection of an instantaneous sample, the cylinders provide information on the air quality at the time and location of sampling. Orbiter air was sampled before and during each flight using separate cylinders. The in-flight air sample was collected on the final flight day in order to provide information on the types of chemical species that had been present in the Orbiter. During STS-40, a situation arose in the Orbiter middeck in which it was necessary to collect an extra air sample using the contingency bottle. Spacelab air was collected three times during both missions. Preflight, Orbiter in-flight, and Spacelab in-flight air sampling cylinders were returned to the JSC Toxicology Laboratory and analyzed quantitatively for trace amounts of hydrogen, methane, and carbon monoxide by GC. A more extensive analysis for the detection and quantitation of volatile organic compounds was then performed using a GC/MS.

2.1.2 Solid Sorbent Air Sampler (SSAS)

The SSAS contains eight sorbent tubes that trap and concentrate volatile organic contaminants from the Shuttle atmosphere. As 3 L of air is pumped through the sorbent tube, air contaminants are selectively adsorbed onto Tenax-GC over a known sampling period (typically 24 hours). The SSAS gives an average concentration of contaminants present in the Shuttle as opposed to the instantaneous measurement that the sampling cylinders provide. During the missions, the SSAS unit collected air samples over 7 24-hour periods. Compounds trapped on the Tenax sorbent resin were thermally desorbed and introduced into a GC/MS for detection and quantitation. For the more volatile contaminants, retention volume correction factors obtained from the literature were applied to their measured concentrations in order to estimate the actual concentration.[6]

2.1.3 Data Analysis Methods

The quality of the Shuttle breathing atmosphere may be assessed in terms of a collective toxicity potential (T-value) for all volatile air contaminants present in the Shuttle. The T-value for total air contaminants is estimated by adding ratios of each component concentration (C) to its 7-day spacecraft maximum allowable concentration (SMAC) as illustrated below:

$$T = C_1/SMAC_1 + C_2/SMAC_2 + \ldots C_n/SMAC_n$$

Air containing contaminant mixtures summed to give a T-value below 1.0 is toxicologically acceptable to breathe at the time and location of sampling. For air mixtures having a T-value > 1.0, the contaminant concentration exceeds that of the 7-day SMAC and air quality may be unacceptable for breathing.

2.2 PARTICULATE MATERIAL

2.2.1 Reference Standard Analyses

To prepare for the Orbiter/Spacelab debris analyses, reference standards, such as soiless media (STS-42; Gravitational Plant Physiology Facility), rat hair, food bar, and feces (STS-40; Animal Enclosure Module {AEM} and Rodent Animal Holding Facility {RAHF} animal housing facilities) were received for chemical analysis and were representative of materials contained in the Spacelab experiments. Reference pyrolysis spectra for each standard were obtained by PY-GC/MS for later comparison with the unknown debris particulates.

2.2.2 Shuttle Filter Debris

Orbiter and Spacelab debris were received for

microscopic and chemical analysis. The Orbiter debris was collected twice during the mission by vacuums of the 24 filters located in the flightdeck, middeck, and middeck overhead; all debris collected from these vacuums was placed in one bag. Spacelab debris was collected during postflight vacuuming of the filters.

Orbiter debris, which was received in vacuum bags, was separated into lint/hair and particle fractions; Spacelab debris was received pre-separated. The loose particles were observed under a dissecting microscope. Particles visually resembling the reference standards were collected from the debris, photographed, and placed in individual vials. To prepare for analysis, particles from each vial were placed in a sample crucible and weighed on a microbalance. Sample weights varied, depending on the type and number of particles (food-like particles, 200-250 μg; plant material, 40-80 μg). The particles, which were typically in the 300-500 μm diameter range, were then analyzed by PY-GC/MS. The unknown pyrolysis spectrum obtained by PY-GC/MS was then compared with the reference sample spectrum for identification.

2.3 MICROBIOLOGY

2.3.1 Microbial Air Sampler (MAS)

Microbiological air samples are typically collected early in the mission, midmission, and late in the mission from the Orbiter flightdeck and middeck, and the Spacelab. Using the principle of air centrifugation, the MAS draws in air containing bacteria and fungi, and the air is then exposed to agar-medium strips. Two strips were exposed at each sampling location; one strip is specific for bacteria (trypticase soy agar), and the second strip is specific for fungi (rose bengal agar). After exposure, the agar-medium strips were returned to the JSC Microbiology Laboratory for analysis. Following incubation of the strips, the microbial colonies that formed were counted and reported as colony-forming units (CFU) per cubic meter of air.

3.0 RESULTS

3.1 VOLATILE CONTAMINANT CONCENTRATIONS

3.1.1 Sampling Cylinders

Highlights of the STS-40/42 Spacelab cylinder air analysis are reported in Table 1. Only volatile contaminants having the highest concentrations are shown in Table 1; however, all contaminants detected and quantified in the cylinder samples were used in the T-value calculation. Probable sources for the volatile contaminants are shown in parentheses. Although numerous contaminants were identified, the air was toxicologically safe to breathe with T-values of 0.20, 0.13, 0.21, 0.09, and 0.10.

Orbiter air was sampled on the final flight-day of both missions. However, these samples were not representative of Orbiter air because of low or nonexistent methane and hydrogen concentrations (these metabolic by-products are known to build-up during the mission); the results are therefore not reported.

An additional STS-40 Orbiter cylinder was used to sample air from the Orbiter Refrigerator/Freezer (OR/F) interior as it was producing noxious odors. However, apparently safe contaminant levels (T-value = 0.05) were indicated for the contaminants found. An analysis of contaminants released by the OR/F into middeck air was conducted after the mission to explain the urine-like and aldehydic odors reported by crewmembers. Careful postflight disassembly of the OR/F revealed that an evaporator-fan motor had overheated and was still releasing formaldehyde, ammonia, and possibly hydrogen chloride from polymers that had been heated to at least 180 °C during the mission. Infrared spectroscopy and detector-tube analysis of the vapors produced by the failed motor several days after the mission

Table 1
Analytical Results of STS-40/42 Spacelab Cylinder Air Samples

CHEMICAL CONTAMINANT (concentrations in mg/m^3)	STS-40 0/23:49	STS-40 5/00:57	STS-42 0/03:45	STS-42 4/03:15	STS-42 7/05:45
Halogenated Aliphatics & Aromatics					
trifluorobromomethane (fire extinguishant)	0.01	0.17	14	1.6	6.5
trichlorofluoromethane (offgas)	0.02	0.20	0.18	0.09	0.07
dichloromethane (offgas)	0.18	0.39	0.19	0.39	0.25
Hydrocarbons					
methane (metabolic)	7	46	ND	4	15
toluene (offgas)	0.76	0.03	0.12	0.04	0.11
Ketones					
acetone (offgas,metabolic)	0.54	0.35	0.53	0.73	0.39
Alcohols					
isopropyl alcohol (utility)	7.5	3.8	6.3	1.0	4.3
ethyl alcohol (utility)	0.85	1.64	ND	1.2	1.5
Inorganic Gases					
hydrogen (metabolic)	ND	5.0	ND	1.8	2.3
Miscellaneous					
hexamethylcyclotrisiloxane (offgas)	0.08	0.40	0.78	0.08	0.70
TOTAL T-VALUE	0.20	0.13	0.21	0.09	0.10

confirmed the presence of these contaminants.[7]

3.1.2 Solid Sorbent Air Sampler (SSAS)

Because of the greater volume of air sampled by the SSAS, detection limits are decreased, and consequently additional trace contaminants were collected on the sorbent tubes. Although 52 STS-42 and 108 STS-40 volatile contaminants were detected, only contaminants having the highest concentration and common to both missions are shown in Table 2. Seven out of eight STS-42 SSAS tubes were analyzed, each giving combined toxicity potentials (T-values) varying from 0.16 to 0.26 for Spacelab air. For STS-40, the six SSAS tubes analyzed yielded T-values of 0.06 to 0.15 for contaminants detected in the Orbiter middeck. These low toxicity values indicate that the contaminants retained by the SSAS were well below toxic concentrations.

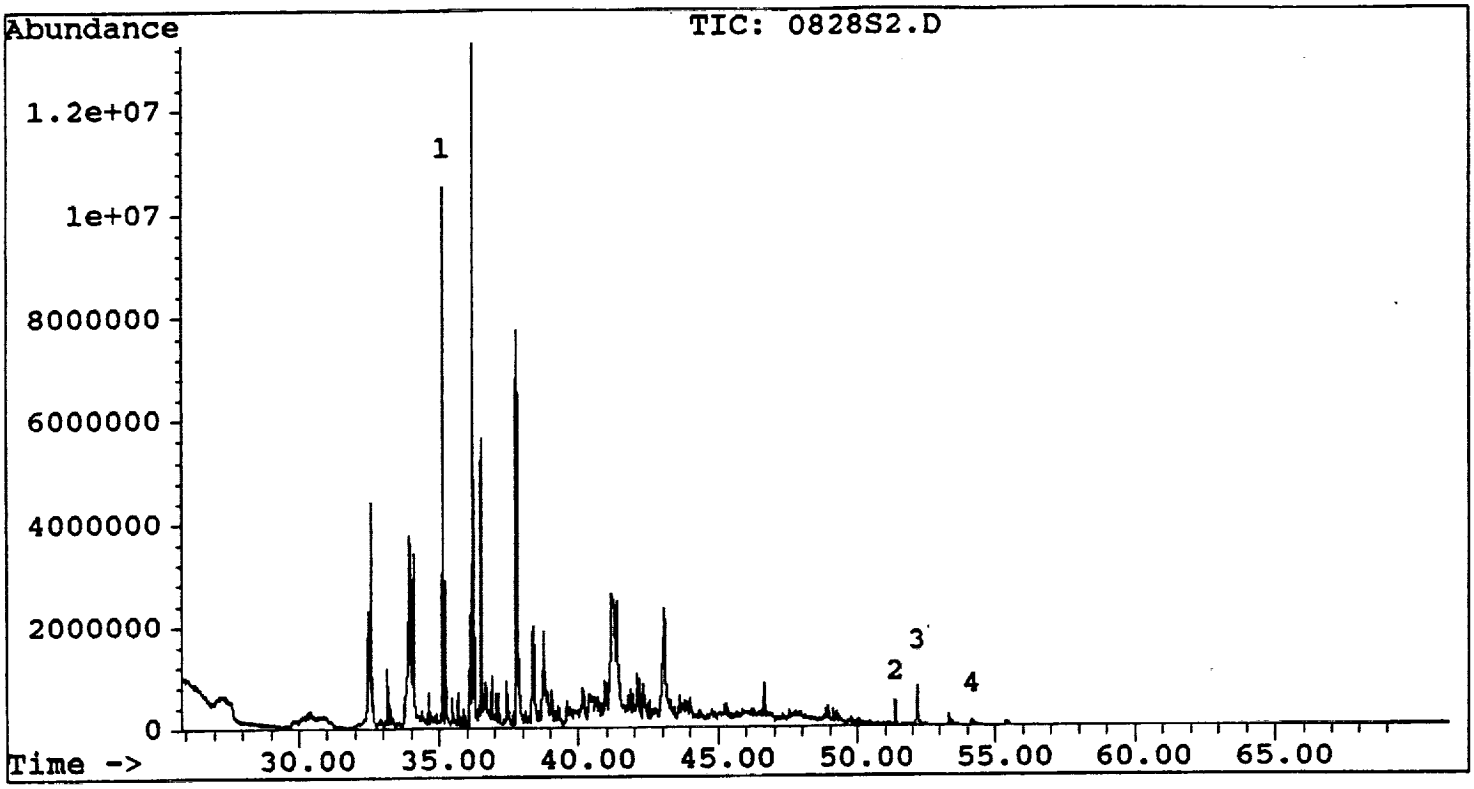
3.2 PARTICULATE MATERIAL

3.2.1 Shuttle Filter Debris

In order to determine if collected particles from the filter debris originated from the Spacelab experiments, the unknown and reference pyrolysis spectra were compared. Reference spectra "marker" compounds were checked against the unknown spectrum to determine if a match existed. The utility of the technique is illustrated in Figure 1, in which a rat food bar pyrolysis spectrum appears to match that of a filter debris particle. Most unknown particulates required chemical analysis for identification; however, rat

Figure 1
Comparison of Pyrolysis Spectra of Spacelab Particle (A) and Rat Food Bar Reference (B)

a



b

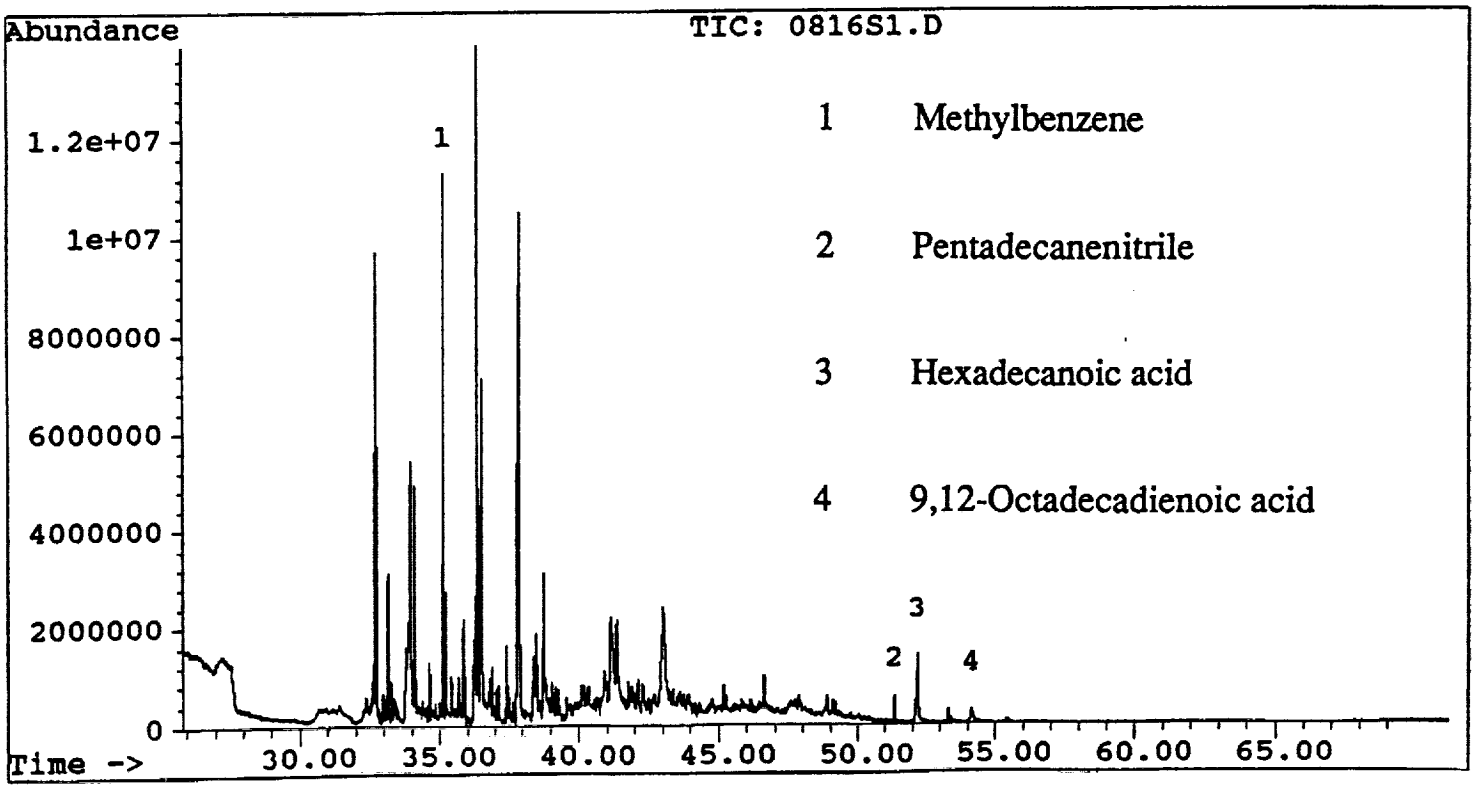


Table 2
Analytical Results of In-Flight STS-40/42
Solid Sorbent Air Samples

CHEMICAL COMPOUNDS (concentrations in mg/m^3)	STS-40	STS-42
Halogenated Compounds		
trifluorobromomethane +	0.1-3.5	16-22
1,1,2-trichloro-1,2,2-trifluoro-ethane +	0.6-2.5	0.1-0.6
trichlorofluoromethane +	1.2-8.7	0.2-1.2
dichloromethane ++	0.2-0.8	0.3-0.6
Hydrocarbons		
2-methyl-1,3-butadiene +	0.1	0.1
Ketones		
acetone	0.2	1.0-1.4
Alcohols		
isopropyl alcohol +	0.5-1.2	3.4-5.9
ethyl alcohol +	1.6-4.3	0.8-5.1
2-methyl-2-propanol ++	0.1	0.1-0.4
Miscellaneous		
hexamethylcyclotrisiloxane	0.1	0.1-0.2
TOTAL T-VALUE	0.1-0.2	0.2-0.3

+ Retention volume corrected values reported
++ STS-40 retention volume corrected values only

hairs in the Spacelab debris were positively identified by microscopic analysis using a compound microscope with 200x magnification and phase contrast.

Particle analysis results, both microscopic and chemical, are summarized for STS-40 and 42 in Table 3. A smaller subset was selected from the original debris to serve as an estimate for overall component levels in the total sample. Percentages of each filter debris component relative to the total number of particles in a group were estimated for the Orbiter and Spacelab filters. The percentage by weight of each component was not taken into account in these estimates, but particle diameters typically ranged from 100-500 µm. Of the animal-related particulates, rat food bar and rat hair were detected in the Spacelab filter debris in trace amounts. A trace amount of soiless media was detected in the Spacelab debris.

3.3 MICROBIOLOGY

3.3.1 Microbial Air Sampler

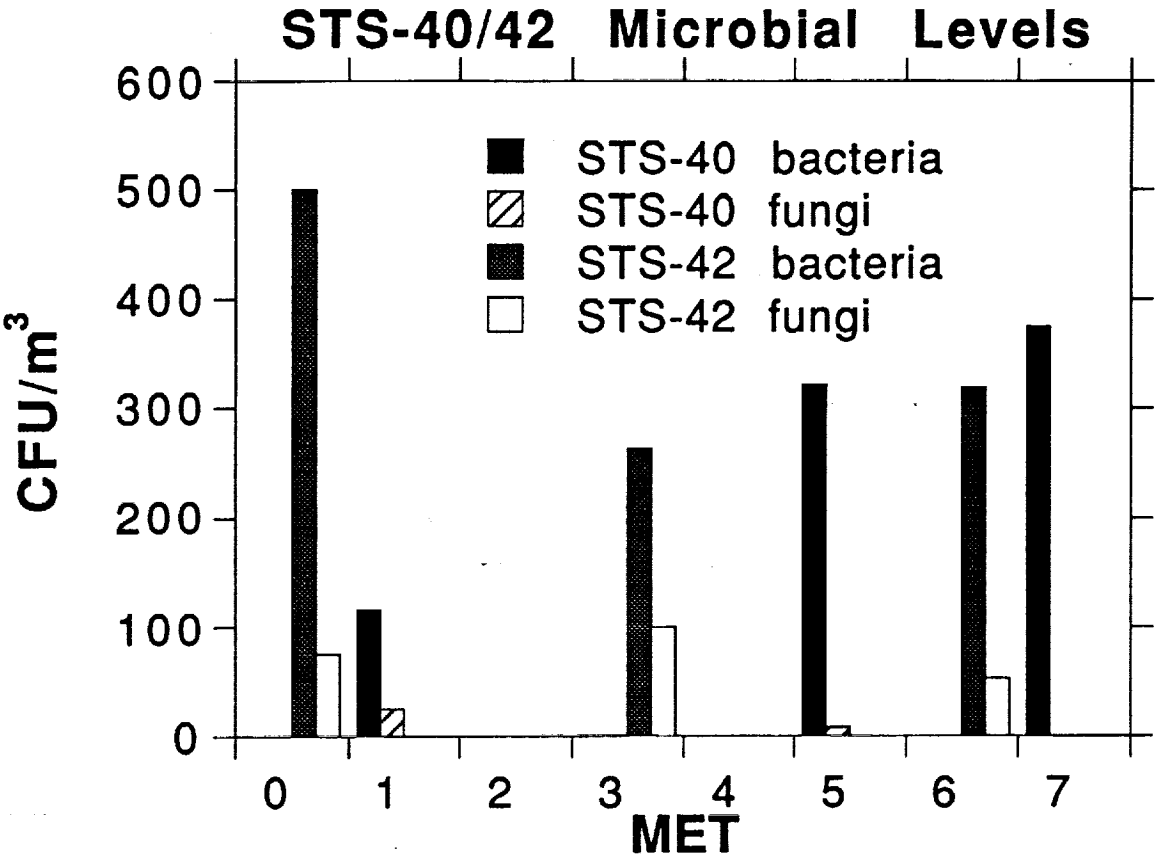
The results obtained from the STS-40/42 MAS samples are given in Figure 2. For each sample day during STS-40, results from the three sampling locations (Orbiter flightdeck and middeck, Spacelab) were averaged to give the mean concentrations of bacteria and fungi. As the mission progressed, airborne levels of bacteria seemingly appeared to increase. The bacterial mean increased from 120 CFU/m^3 on day 1 to 375 CFU/m^3 on day 7. For STS-42, samples were collected on the middeck and flight deck on days 1, 3, and 6, but Spacelab samples were collected only on day 6. This data did not show the typical increase in bacteria as a function of mission duration. For both missions, bacteria were more prevalent than fungi, which is typically observed.

Table 3
Estimate of Debris Particle Levels

	Orbiter Filter Debris		Spacelab Filter Debris	
	STS-40	STS-42	STS-40	STS-42
Rat hair	-	N/A	+/-	N/A
Rat feces	-	N/A	-	N/A
Rat food bar	-	N/A	+/-	N/A
Soiless media	N/A	-	N/A	+/-

+/- = < 1% - = Nondetectable

Figure 2



4.0 DISCUSSION

4.1 VOLATILE CONTAMINANTS

Fifty-two volatile contaminants were collected on the SSAS sorbent tubes from the STS-42 Spacelab atmosphere; 108 contaminants were detected in the STS-40 Orbiter middeck. Although fewer compounds were detected during STS-42, the SSAS T-values for this mission were generally higher than those obtained for STS-40 contaminants. STS-40 T-values for individual tubes were 0.15, 0.09, 0.13, 0.06, 0.09, and 0.12, whereas STS-42 values were 0.17, 0.16, 0.22, 0.21, 0.23, 0.20, and 0.26. Therefore, on the average, higher concentrations of contaminants were released into the STS-42 Spacelab atmosphere. However, the T-values for both missions are well below the toxicity potential limit of 1.0, thus indicating toxicologically safe breathing atmospheres.

Although toxicity levels were generally acceptable throughout the STS-40/42 missions, a problem midflight with the OR/F temporarily produced some noxious odors during STS-40. Since these odors caused irritation and nausea in some crewmembers, the source of the odors and the chemicals eliciting the symptoms were investigated by postflight analysis of OR/F components. It was determined that the source of the noxious odors was thermodegradation of polymers in and adjacent to an overheated evaporator-fan motor. Thermodegradation of polymers

may release toxic gases by production of the monomeric unit or elimination of small molecules, such as hydrogen chloride.[8,9] In the case of the OR/F components, the major thermodegradation contaminants causing the symptoms were ammonia, formaldehyde, and possibly hydrogen chloride. Since these contaminants are reactive and are not amenable to GC/MS detection, they were not detected in the bottle sample.

4.2 PARTICULATE MATERIAL

PY-GC/MS chemical analysis was successful in identifying the source of most food-related and plant-like debris particles. Definite matches of unknown debris particles with reference rat food bar and soiless media particles were observed, illustrating the utility of chemical analysis in determining the identification and source of debris particles. Moreover, the combination of microscopic and chemical techniques demonstrated that trace amounts of contaminants from Spacelab experiments were present in the cabin atmosphere. The animal containment facilities (AEM and RAHF) appeared to be effective in containing animal-related particulates, since no rat fecal material was positively identified and only small amounts of rat hair and food bar were detected in the Spacelab air filters. In addition, the GPPF experiment successfully contained soiless media particles; only a trace amount of soiless media was detected in the Spacelab cabin filter.

4.3 MICROBIOLOGY

A general increase in the number of airborne bacteria was observed as a function of mission duration on STS-40. This trend has been observed on some previous flights, but was not observed on STS-42. For both missions, the types and levels of bacteria were similar to those values found in a typical office space. Overall, the crew was not exposed to any unusual microbial risk via the airborne route.

5.0 CONCLUSION

A comprehensive air analysis study of the STS-40/42 Orbiter/Spacelab atmosphere was performed, providing information on the types and degree of contamination present in the Shuttle environment. Based on the analysis of Orbiter and Spacelab atmospheric "grab" samples collected during these missions, the air was toxicologically safe to breathe except during STS-40 when the OR/F was releasing noxious gases into the middeck. During STS-40, it appears that with an increase in mission duration, there was a possible bacterial build-up. This trend was not observed for STS-42. However, the low levels of microbial contaminants in samples collected during the missions indicate that the crew was not exposed to any unusual microbial risk. Chemical analysis of particles collected on Shuttle filters enabled the identification of particles and their source. The STS-40 Orbiter/Spacelab air was free of rat fecal particulates, but small amounts of rat hairs and food bar particles were found in the Spacelab air filters. A trace amount of soiless media was detected in the STS-42 Spacelab cabin filter. The low levels of animal-related and plant-like particles found in the Spacelab filters indicates that the containment for these Spacelab experiments is effective.

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